The Unimolecular Elimination Kinetics of Benzaldoxime in the Gas Phase

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ABSTRACT: The kinetics of the gas-phase elimination of benzaldoxime was determined in a static reaction system over the temperature and pressure range 350°C–400°C and 56–140 Torr, respectively. The products obtained were benzonitrile and water. The reaction was found to be homogeneous, unimolecular, and tend to obey a first-order rate law. The observed rate coefficient is represented by the following Arrhenius equation:

 $\log k_1(s-1) = (12.00 \pm 0.19) - (188.0 \pm 2.3)$ kJ mol⁻¹(2.303 RT)⁻¹

According to kinetic and thermodynamic parameters, the reaction proceeds through a concerted, semi-polar, four-membered cyclic transition state type of mechanism. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 145–147, 2007

INTRODUCTION

There are few reported research works on the thermal decomposition of oximes. The pyrolysis kinetics of formaldoxime [1], at 350°C to 415°C, was found to produce hydrogen cyanide and water [reaction (1)] and tend to obey a first-order rate law.

$$CH_2NOH \xrightarrow{\Delta} HCN + H_2O$$
 (1)

Years later, Pratt and Purnell [2] carried out the pyrolysis of acetaldoxime. The reaction was somewhat heterogeneous, showing some induction period, and the mechanism was described as a free radical process [3]. In 1967, camphor oxime was pyrolyzed at two different temperatures [4]. When pyrolyzed at 240°C for 6–7 min and distilled under reduced pressure, it yielded three products as described in reaction (2). When pyrolysis was carried out in vapor phase at 500°C for 1 s, the main product was found to be 1,2-dimethyl-3-cyanomethylcyclopentene [reaction (2)].



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In view of the little information regarding pyrolysis of oximes in the gas phase, this work aimed at examining the homogeneous elimination kinetics of benzaldoxime in the gas phase, and to consider a reasonable mechanism, if possible.

EXPERIMENTAL

The starting material benzaldoxime (Aldrich) of 98.0% purity was used (GC-MS: Saturn 2000, Varian 3600X, with a DB-5MS capillary column 30 m × 0.25 mm i.d., 0.25- μ m film thickness). The quantitative chromatographic analysis of benzonitrile product was determined by using a Gas Chromatograph Hewlett Packard 5710-A with a 10% SP-1200, 1% H₃PO₄ Chromosorb WAW 80–100 mesh, 2 m. The identification of the benzonitrile product was made by comparing with true authentic samples bought from Aldrich (GC-MS: Saturn 2000, Varian 3600X with a DB-5MS capillary column 30 m × 0.25 mm i.d., 0.25- μ m film thickness).

Table IRatio of Final (P_f) to Initial (P_0) Pressure forthe Substrate Benzaldoxime

Temperature (°C)	P_0 (Torr)	$P_{\rm f}$ (Torr)	$P_{\rm f}/P_0$	Average
360	48	94	1.9	2.0
370	70	135	1.9	
380	57.3	114.3	2.0	
390	57.4	113.4	2.0	
400	37.2	74.2	2.0	

Table IIIHomogeneity of the Elimination Reactionsfor Substrate Benzaldoxime at 380.5°C

$S/V (\mathrm{cm}^{-1})^a$	$10^4 \times k_1 \ (\mathrm{s}^{-1})^b$	$10^4 \times k_1 \ (\mathrm{s}^{-1})^c$		
1	9.60 ± 0.22	9.50 ± 0.30		
6	9.54 ± 0.24	9.51 ± 0.14		

^{*a*} S =surface area; V = volume.

^b Clean Pyrex vessel.

^c Vessel seasoned with allyl bromide.

Table IVEffect of Free Radical Inhibitor Toluene onRates for Substrate Benzaldoxime at 380.0°C

P ^a _s (Torr)	P _i ^b (Torr)	$P_{\rm i}/P_{\rm s}$	$10^4 \times k_1 ({ m s}^{-1})$
42.9	_	_	9.52
61.8	69	1.1	9.50
56.7	69	1.2	9.32
57.3	85	1.5	9.40
54.9	86	1.6	9.40
42.1	85	2.0	9.32
41.1	100	2.4	9.51

 ${}^{a}P_{s} = \text{pressure substrate.}$

 ${}^{b}P_{i} = \text{pressure inhibitor.}$

Table VInvariability of the Rate Coefficients WithInitial Pressure for Substrate Benzaldoxime at 370°C

Parameter	Value					
P ₀ (Torr)	61	70	72.5	85		
$10^4 \times k_1 \ ({ m s}^{-1})$	5.40	5.30	5.35	5.25		

Kinetics

The reaction kinetics was studied in a static reaction system as described before [5–7]. At each temperature, 6 to 9 runs were carried out. The rate coefficients for the benzaldoxime decomposition was calculated manometrically from the pressure increases. The temperature was maintained within $\pm 0.2^{\circ}$ C through control with a Shinko DIC-PS 23TR resistance thermometer and was measured with a calibrated iron–constantan thermocouple. No temperature gradient was observed along the reaction vessel. The substrates were all injected directly into the reaction vessel with the help of a

Table II Stoichiometry of the Reaction for Substrate Benzaldoxime at 390.0°C

Parameter				Value				
Time (min)	5	7	9	11	16	20	30	40
Reaction (%) (pressure)	11.2	20.0	25.3	30.0	38.6	42.6	57.3	68.5
Benzonitrile (%) (GLC)	11.4	19.2	25.9	30.5	37.7	41.1	55.2	67.2

Parameter		Value				
Temp. (°C) $10^4 \times k_{\rm c} (c^{-1})$	350.4 1.75 ± 0.07	360.8	370.2 5 48 ± 0.03	380.1	390.4	400.1
$\frac{10 \times k_1(s)}{a}$	1.75 ± 0.07	3.36 ± 0.11 $0 \pm 0.19) = (188.0 \pm 0.11)$	5.46 ± 0.05	9.36 ± 0.10 $3RT)^{-1} r = 0.9997$	15.32 ± 0.02	20.44 ± 0.01

Table VI The Variation of the Rate Coefficients With Temperatures for Substrate Benzaldoxime^a

Table VII Kinetic and Thermodynamic Parameters at 370°C for Substrate Benzaldoxime

$k_1 \times 10^4 (\mathrm{s}^{-1})$	$E_{\rm a}$ (kJ mol ⁻¹)	$\log A \ (\mathrm{s}^{-1})$	$\Delta S^{\ddagger} (\text{J mol}^{-1} \text{ K})$	ΔH^{\ddagger} (kJ mol ⁻¹)	$\Delta G^{\ddagger} (\text{kJ mol}^{-1})$
5.34 ± 0.03	188.0 ± 2.3	12.00 ± 0.19	-29.9	182.7	201.9

syringe through a silicone rubber septum. The amount of substrate used for each reaction was approximately 0.05–0.1 mL.

RESULTS AND DISCUSSION

The unimolecular elimination of benzaldoxime in the gas phase is described by reaction (3). The stoichiometry of this reaction demands for a long reaction time, $P_f/P_0 = 2.0$,



where $P_{\rm f}$ and P_0 are the final and initial pressures, respectively. The average experimental $P_{\rm f}/P_0$ at five different temperatures and 10 half-lives was 2.0 (Table I).

The stoichiometry of reaction (3), up to 68% decomposition, was checked by comparing the extent of decomposition of the substrate from pressure measurements with that obtained from quantitative GLC analyses of benzonitrile formation (Table II).

The pyrolytic elimination of reaction (3) was found to be homogeneous, since no significant variations in rates were obtained when using both clean Pyrex and allyl bromide seasoned vessels with a surface-tovolume ratio of 6.0 times greater than normal, which is equal to 1.0 (Table III). The rates were not affected by the effect of different proportions of toluene inhibitor (Table IV). No induction period was observed and the rates were reproducible with a relative standard deviation of no more than 5% at a given temperature.

The rate coefficient for elimination reaction from $k_1 = -(2.303/t) \log[(2P_0 - P_t) - P_0)]$ was found to

be independent of the initial pressure (Table V), and the first-order plots of $\log(2P_0 - P_t)$] against time *t* are linear up to 68% of the reaction. The variation of the rate coefficients with temperature and the corresponding Arrhenius equation are shown in Table VI, where 90% confidence limits from a least-squares procedure are given.

Data from Tables I to VI and the kinetic and thermodynamic parameters given in Table VII imply reaction (3) to be molecular in nature. Apparently, the N–OH bond polarization, in the sense $N^{\delta+} \cdots OH^{\delta-}$, is rate determining. Then, the $OH^{\delta-}$ may abstract the benzylic hydrogen to yield benzonitrile and water through a concerted four-membered cyclic transition state type of mechanism, as described in reaction (4)



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